

PORLAND-ZEOLITE-CEMENT FOR MINIMIZING ALKALI-AGGREGATE EXPANSION

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ABSTRACT

The Authors give an account of the performance modifications induced in the blended cements by replacing the typical pozzolanas with their zeolitic counterparts: volcanic tuffs, after suitable grinding. The advantages of such a replacement in terms of minimization of alkali aggregate expansion and of strengths increase at long ages are discussed, emphasizing also the favourable influence of expansion abatement supplied by a previous thermal treatment of the zeolitic addition. The improved strength progress is interpreted in terms of a higher reactivity of the zeolite minerals in comparison with that of the pozzolanic glass and the expansion abatement in terms of ability to incorporate high alkali amounts showed by the abundant amorphous hydrated silicate.

Introduction

The suitability of minimizing alkalis reaction with some siliceous constituents, sometimes present as impurities in the aggregates for concrete, has recently been the more to the fore in Italy, too, owing to certain concurrent factors. They are substantially: the increased cost of thermal unit, favouring the choice of technologies which cause an alkali rise in the clinker (1); the return of dusts in the kiln, for environmental protection, before their immission to stack, which interferes with alkalis removal; the progressive exhaustion of the quarries better studied from the geo-mineralogical standpoint and the consequent use of less investigated aggregates; the advantage of employing aggregates to be found at hand.

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ion due to the neoformation of an alkaline jellylike silicate can be reduced, as is well known (2), by partial replacement of Portland clinker with suitable active additions, such as: pozzolanas, fly ashes, blastfurnace slags, etc. In order to cut down expansion, without detriment to early ages and strength (3), it is therefore imperative to carefully individuate the type of active addition.

EXPANSION

As result of a long and systematic investigation devoted to examining thoroughly the manifold aspects of the partial replacement of clinker with the zeolitic counterparts of the true pozzolanas: the volcanic tuffs (4), we are able to present a type of "pozzolanic" cement prepared by partial replacement of clinker with those tuffs, which is definitely suitable for remarkably reducing or indeed removing, if manufactured with thermal activated zeolitic tuff, the harmful expansion even with high alkali clinkers (5). The structure and technical performance of such a cement are described in detail.

Experimental

Tuffs, collected in various National eruptive districts and different geological periods, and content of zeolite minerals diffused in their matrix, have been determined, after suitable grinding, for partial replacement of Portland clinker. Mineralogical composition of the products used is reported in Tab. I. Pozzolanas n. 4 (leucitic type) and n. 6 (alkali-trachytic type) are the vitreous parts of Roman tuffs n. 1 and 3 (low and high Latium) and Neapolitan tuff n. 5, respectively. Zeolite minerals amount has been calculated on the basis of water content. A detailed account of the mineralogical composition and characterization of the above mentioned tuffs is reported in previous papers (6), (7), (8), (9).

Industrial gypsum has been added to a clinker (Tab. I) having $395 \text{ m}^2/\text{kg}$ Blaine surface area. The additions have been in turn ground until a $13 \pm 4\%$ residue remains on a $32 \mu\text{m}$ sieve. Then blended cements have been manufactured in laboratory by mixing the clinker with 10, 20, 40% of each addition, as it is known after one hour's thermal activation treatment (1) at 500°C .

It is ascertained, by means of the pozzolanicity test according to Italian specifications (10), that all the blended cements prepared definitely belong to the pozzolanic type when clinker replacement exceeds 10%, the tests here summarized have been performed.

The author emphasizes the influence of each addition, thermally activated or not, on the workability of fresh mix, determined as resistance to the flow of a concrete, according to ASTM C 230-80 Specification. The graphic design of the results obtained indicates that moderate clinker replacements most of all increase the mixes workability, which, however, definitely decreases as replacement increases. It is to be noticed also that zeolitic additions lower workability in a slightly higher way than the vitreous counterparts and that the workability goes slightly down again if the addition has been previously activated.

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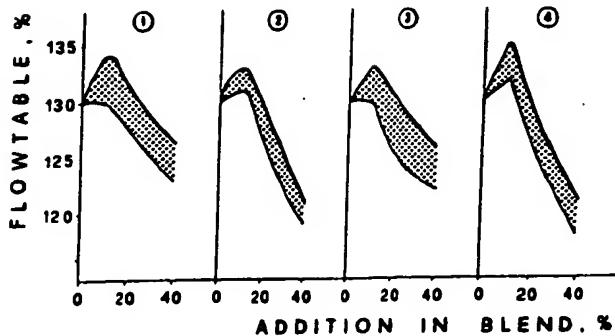
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TAB. 1
Chemical composition of the active additions (weight %)

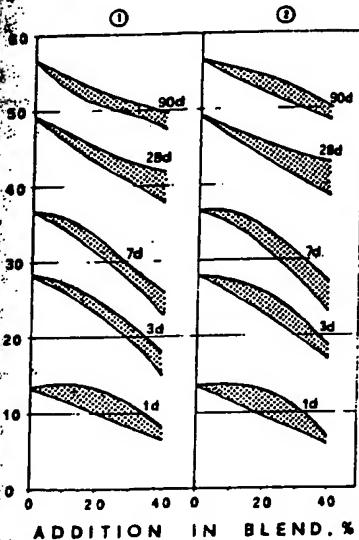
Sample number	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	1.0.1.
1 tuff	42.0	15.9	9.0	13.0	4.0	0.5	5.4	10.1
2 pozzolan	43.3	17.4	9.0	13.4	3.9	0.5	5.9	6.5
3 tuff	50.1	18.7	4.6	5.2	1.2	1.1	5.9	13.5
4 pozzolan	54.1	20.9	4.7	4.4	1.5	2.3	6.2	5.8
5 tuff	54.6	17.7	4.1	3.6	0.9	3.4	6.3	9.1
6 pozzolan	57.0	18.3	4.5	3.1	0.9	4.1	8.0	3.7
clinker chemical and potential phase composition								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Na_2O eq.
21.3	3.6	4.5	65.3	1.0	0.7	1.7	2.1	1.8

$\text{C}_3\text{S} = 63\%$; $\text{C}_2\text{S} = 13\%$; $\text{C}_4\text{AF} = 14\%$; $\text{C}_3\text{A} = 2\%$.

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Variation bands of flow values as a function of per cent addition.
Mortars manufactured with blended cement containing:
(1) pozzolanas, (2) activated pozzolanas, (3) tuffs, (4) activated
tufts.



Variation bands of compressive strength
values as a function of per cent addition
and curing period. Mortars manufactured
with blended cements containing: (1) poz-
zolanas, (2) activated pozzolanas.

Fig. 2 and 3 answer for
the results of the compres-
sive strength tests on
standard mortars (11)
manufactured with pozzolan-
and with tuff-cement sam-
ples. The graphic design
of the data obtained,
as a function of addition
amount (activated or not)
and curing period, empha-
sizes the favourable in-
fluence of the zeolitic
addition in terms of miti-
gation on the long ages
strength decrease, too.
It is to be noted also
that activation treatment
of any type of addition
does not effect very much
compressive strength of
the mortars.

Fig. 4 reports the results
of potential alkali reactiv-
ity, performed on mortar

prepared using Pyrex glass as aggregate, according
to TM C 441-81 Specification. Data after six months curing show the remarkable
influence of the zeolitic addition on expansion abatement. Such a positive
influence is increased the more if the zeolitic addition has been thermally
activated. After activation, the zeolitic addition in suitable amount in princi-
ples removes the expansion, in comparison with the Portland cement, whereas

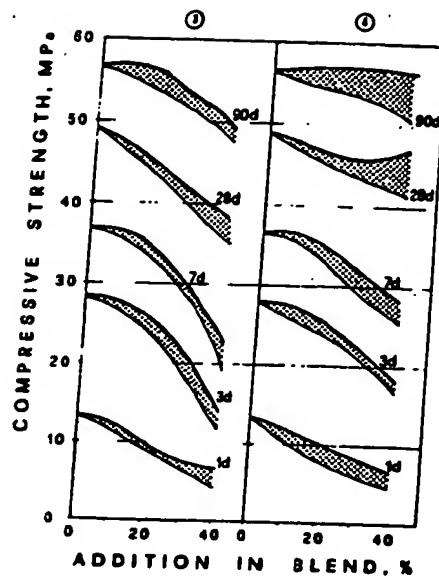


Fig. 3. Variation bands of compressive strength values as a function of per cent addition and curing period. Mortars manufactured with blended cements containing: (3) tuffs, (4) activated tuffs.

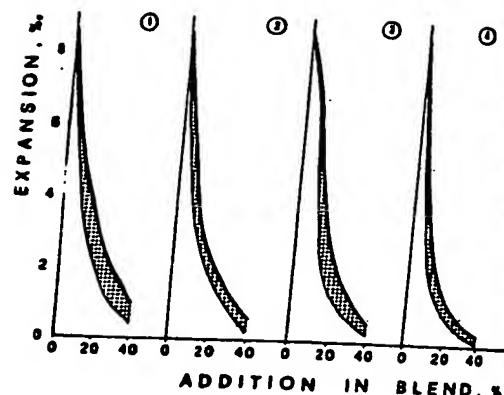


Fig. 4. Variation bands of expansion values as a function of per cent addition. Mortar bars manufactured with blended cements containing: (1) pozzolanas, (2) activated pozzolanas, (3) tuffs, (4) activated tuffs.

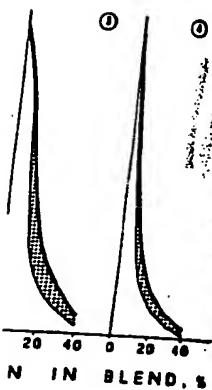
the same results can be reached adding a remarkably higher amount of vitreous counterparts.

Discussion and Conclusion

The whole of the experimental results indicate that the partial replacement of clinker with zeolithic additions allows the preparation of blended cements with technical performance better than that of the typical pozzolanic cements manufactured with the vitreous counterparts. Such an improved performance appears in terms both of compressive strength and of minimization of alkali aggregate expansion. Expansion appears moreover the lower if the zeolithic addition has been previously activated by one hour's thermal treatment at 500°C, whilst there is no evidence of such a further abatement after the same treatment of the vitreous counterparts. At this point it is to be noted that the advantage related to the physical state of the typical incoherent pozzolanas, in comparison to the lithic zeolithic counterparts, is more apparent than effective, since energy consumption for grinding operation does not differ very much for both the products, owing to the peculiar fine-grained texture of the zeolithic tuffs (7). The grinding

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of the two products demands in fact about 8-10 Kwh/ton, in comparison with the 30 Kwh/ton requested by the clinker, and the drying operation of the clinkers or of a tuff, demands 200-250 Kcal/kg.

The decrease of workability induced in the mixes by the zeolithic nature of the addition and the related higher water amount requested, does not influence the mechanical performance. Workability, in any case, can be suitably improved by means of water reducing agents.

and phillipsite, representing the main zeolithic minerals to be found, in small amounts, in the matrix of Italian volcanic tuffs, are definitely conceivable as active additions to Portland clinker.

In presence of alkali reactive aggregates, zeolithic additions allow the production of clinkers with alkali content highly exceeding the Na₂O eq. limit of ASTM Specification, according with the advancement of production technologies.

The case of compressive strength, as well as the increased aptitude for expansion due to alkali aggregate reaction, are both to be interpreted on the basis of a higher reactivity of the zeolite products towards comparison with that of the vitreous counterparts. Owing to the peculiar crystalline structure of porous solids exhibited by zeolite minerals, the specific surface area wider than that of the bubbly pozzolanic glass is due to the attack of alkaline solution, so favouring a more rapid and complete Si-O-break, as a consequence of the attack of lime solution, causes, in the neoformation of abundant, low basic, amorphous hydrated calcium which, favouring a more rapid compressive strength progress, can, at the same time, incorporate remarkable alkalis amount, that otherwise would be liable for fostering the dangerous expansion reaction.

Other expansion abatement supplied by thermal activation of the zeolithic minerals can in turn be interpreted on the basis of the following concurrent processes: the formation of free bonds at the surface of the solid, owing to the evolution from its pores and channels; a sort of mobilization of the species due to the collapse of the crystalline structure; the wide surface are induced in the neoformed amorphous system by the originary crystalline structure of the porous solid.

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